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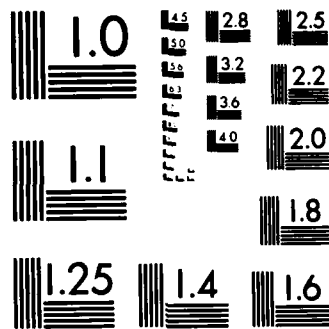
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*Studies of the Correlation of Electrode
Kinetics with Molecular Structure*

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Michigan State University

Principal Investigator: Michael J. Weaver

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A summary of accomplishments includes the following. The electron-transfer kinetics of a number of Co(III)/(II) and Cr(III)/(II) couples attached to mercury, silver, platinum, and gold surfaces via simple inorganic bridging groups has been monitored in order to ascertain how the energetics of electron transfer depend upon the chemical nature of the electrode surface and the structure of the bridging ligands. Comparisons were made with the kinetics of corresponding outer-sphere reactions in both electrochemical and homogeneous reaction environments. These comparisons indicate that the elementary barrier to heterogeneous electron transfer can be significantly lowered by surface attachment, although the catalyses thus induced are somewhat smaller than often found for homogeneous ligand-bridged processes.

Concurrent with these experimental studies, we have developed kinetic formalisms to aid the comparison between experiment and contemporary theoretical models, and to facilitate the analysis of electrochemical kinetic data in a parallel fashion to the sophisticated treatments recently developed for homogeneous electron-transfer processes. In particular, we have formulated a "preequilibrium" treatment of electrochemical processes which enables the kinetics of electrode processes following outer-sphere and inner-sphere (i.e. surface-attached) reaction pathways to be compared on a common basis. We have demonstrated electrochemical activation parameters determined for surface-attached reactants can be utilized to obtain information on the extent of adiabaticity of heterogeneous electron transfer. Application of this analysis to some thiocyanate and thiophenecarboxylate-bridged reductions of Co(III) and Cr(III) demonstrated that the extent of electronic coupling between the surface donor and metal redox acceptor orbitals is strongly inhibited by interruption of bond conjugation in the bridging ligand.

An important new development in the research program has been to utilize SERS to provide molecular-level information on the structure of adsorbates, especially those engaging in electron-transfer reactions. Initial studies have focussed on establishing quantitative relationships between the nature and intensity of the SERS spectra and the interfacial composition of silver-aqueous interfaces determined independently by electrochemical means. These studies have included the quantitative determination of electrode coverage-potential data for a number of structurally simple adsorbed anions and the direct comparison with corresponding SERS intensity-potential for these adsorbates. We have recently reported the first observation of a simple adsorbed redox couple, $\text{Os}(\text{NH}_3)_5$ pyridine(III)/(II), using SERS. These studies are providing hitherto unavailable information on the nature of adsorbate-surface bonding in structurally well-defined electrochemical systems.

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ABSTRACT

The overall objective is to develop our understanding of the connections between the kinetics and mechanisms of heterogeneous electron-transfer reactions at metal-electrolyte interfaces and the molecular structure of the reactant and the interfacial region. We have chiefly focussed attention on transition-metal redox couples, especially Co(III)/(II), Cr(III)/(II), and Ru(III)/(II) containing adsorbing inorganic and organic ligands at a number of electrocatalytic solid surfaces, especially silver, platinum, and gold, as well as at mercury electrodes. By combining electrochemical kinetic and reactant adsorption thermodynamic measurements, along with in situ vibrational spectroscopic studies using Surface-Enhanced Raman Scattering (SERS), the various catalytic influences exerted by the metal interface upon the energetics of electrode reactions have been probed in detail.

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An important new development in the research program has been to utilize SERS to provide molecular-level information on the structure of adsorbates, especially those engaging in electron-transfer reactions. Initial studies have focussed on establishing quantitative relationships between the nature and intensity of the SERS spectra and the interfacial composition of silver-aqueous interfaces determined independently by electrochemical means.^{12,14,16,21,23} These studies have included the quantitative determination of electrode coverage-potential data for a number of structurally simple adsorbed anions and the direct comparison with corresponding SERS intensity-potential for these adsorbates.^{6,16} We have recently reported the first observation of a simple adsorbed redox couple, $\text{Os}(\text{NH}_3)_5$ pyridine(III)/(II), using SERS.²¹ These studies are providing hitherto unavailable information on the nature of adsorbate-surface bonding in structurally well-defined electrochemical systems.

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This report outlines developments in the research program supported by AFOSR under AFOSR-80-0271 from October 1980 - January 1983. This program has been continued since then under AFOSR-83-0011 ("The Molecular Structural Basis of Electrode Kinetics") at the Department of Chemistry at Purdue University. This change coincided with the relocation of the Principal Investigator, Michael J. Weaver, from Michigan State University to Purdue University in the Fall of 1982. Support of this program by AFOSR originated at Michigan State in October 1977. (AFOSR-77-3408). Since the research progress accomplished in the period October 1980 - September 1981 was detailed in the Scientific Report submitted in February 1982, this report will emphasize activities coming to fruition since that time.

PROGRESS SUMMARY

The central unifying theme of this research program is to develop our fundamental understanding of the ways in which the rates and mechanisms of electrode reactions depend upon the structural properties of the reactant and the metal-electrolyte interfacial region in which the reaction occurs. Emphasis has been placed on experimental studies of the electrochemical kinetics and thermodynamics of Co(III)/(II), Cr(III)/(II), and Ru(III)/(II) at a variety of metal surfaces, including mercury, silver, platinum, gold, lead, and "underpotential" deposits of lead on silver. Of particular recent interest is the quantitative examination of the electron-transfer energetics of such reactants when surface attached via either simple inorganic or organic ligands, and the examination of simple ionic adsorbates at electrochemically well-defined silver-aqueous interfaces using Surface-Enhanced Raman Scattering (SERS). An outline of these activities will now be given. The reference numbers refer to the list of publications resulting from AFOSR-80-0271 given below.

I. Electrochemical Kinetics of Redox Centers Adsorbed via Organic Bridges

As noted above, a central ongoing activity of the present research program is to elucidate the various ways in which electron transfer at metal surfaces is influenced by the chemical nature of the redox center and the interfacial structure. In particular, we have focussed attention on "inner-sphere" reactions where the reactant is bound to the metal surface via a bridging group X prior to the electron-transfer step. Incisive insight into the fundamental factors influencing such "electrocatalytic" processes can be obtained for systems where the binding of X to the electrode surface is sufficiently strong so to enable rate constants for the unimolecular electron-transfer step, $k_{et}(\text{sec}^{-1})$, to be measured directly.^{4,7,8,24} Such measurements are directly analogous to the intramolecular electron-transfer kinetics observed for binuclear transition-metal complexes in homogeneous solution. Such electrochemical processes can therefore be usefully considered to involve "surface intramolecular" electron transfer. Comparisons between values of k_{et} measured for a series of related reactions can yield much insight into the underlying structural factors determining the kinetics of electrocatalytic processes.

Our initial studies involved one-electron reductions of cobalt(III) and chromium(III) mediated by simple inorganic bridges, particularly $X = \text{Cl}^-$, Br^- , NCS^- , and N_3^- .^{4,7,8} Aside from the well-defined mercury surface, we have examined silver, platinum, gold, and copper surfaces as model "electrocatalysts." These studies have shown that halide bridges provide the most effective mediating groups, as measured by the increase in k_{et} for the ligand-bridged pathway in comparison with that for the corresponding unbound (outer-sphere) pathway.

Most recently, we have expanded these studies to include a number of reactions mediated by organic bridging ligands.²⁴ Extended organic ligands

are of fundamental interest as bridging groups for several reasons. Firstly, subtle variations can readily be made in the structure of the bridging ligands, enabling detailed insights to be obtained into the mode of electron transfer. Secondly, structural units of widely varying size can be prepared, allowing the ability of the transferring electron to "tunnel" across the separation distance between the reactant redox center and the electrode surface to be examined. Thirdly, organic adsorbates are frequently employed as corrosion inhibitors. It is therefore of practical value to determine their ability to decelerate, as well as accelerate, electrode reactions involving metal ions separated from the surface by such species.

We have recently completed a detailed study of the reduction of pentaamminecobalt(III) bound via a variety of thiophenecarboxylate ligands to mercury, gold or copper surfaces.²⁴ These ligands were chosen since they contain both an effective surface binding group in the thiophene sulfur atom, and a convenient coordinating ligand for Co(III) in the carboxylate group. The structure of the ligand interposed between these two binding groups was altered both by varying the number of carbons between the ring and the carboxylate groups and the ring substitution position. The values of k_{et} were found to be sensitive to the ligand structure, ca. 10-50 fold smaller values of k_{et} being found with thiophenecarboxylates containing one or more saturated carbon linkages interposed between the thiophene and carboxylate moieties. These reactivity patterns, along with the additional observation that the decreases in k_{et} are reflected chiefly in frequency factor decreases rather than increases in the activation enthalpy, provide the first clearent evidence that electrode reactions rates can be limited by electron tunneling, i.e. are "nonadiabatic." A conjugated double-bond system appears to be a

necessary feature of the bridging ligand in order to achieve efficient electron tunneling between the electrode surface and the Co(III) acceptor site.²⁴

Such observations, although the first of their type for electrode reactions, are closely analogous to those made recently for electron transport between metal ions within homogeneous binuclear complexes.

II. Surface-Enhanced Raman Spectroscopy of Electrochemical Interfaces

As noted above, we have recently initiated studies of adsorbates, especially adsorbed reactants, at silver-aqueous interfaces using Surface-Enhanced Raman Spectroscopy (SERS). The overall objective of these studies is to utilize the specific microscopic structural information furnished by SERS to complement the nonspecific thermodynamic, kinetic, and surface compositional information obtained from conventional electrochemical techniques. Instrumentation available for this work includes an optical multichannel analyzer (OMA) system which enables Raman spectra to be obtained repetitively in as little as ca. 20 msec. This allows the progress of electrode reactions involving adsorbed reactants or intermediates to be followed in real time using Raman spectroscopy as well as by conventional electrochemical (current-flow) techniques.

Initial experimental studies of this type were performed in part while the P.I. was on leave of absence at IBM San Jose from September 1981 - March 1982, in collaboration with Drs. J.G. Gordon II and M.R. Philpott of IBM. We have completed two particularly significant studies in the last year or so. Firstly, we have investigated the quantitative relationship between the potential dependence of Raman scattering intensity for simple anionic adsorbates (Cl^- , Br^- , I^- , NCS^- , N_3^- , and CN^-) at silver electrodes with the corresponding potential dependence of the adsorbate coverage.^{16,23} The latter was obtained from differential capacitance data.¹⁶ Generally speaking, roughly linear relationships between

the Raman intensity and the adsorbate coverage were observed provided that the experiments were performed sufficiently rapidly (seconds time scale, using the OMA) so that the microstructure of the metal surface remained constant. These encouraging results represent the first quantitative test of the applicability of SERS as a surface analysis tool in in situ electrochemical systems.

Secondly, we have started to examine the potential-dependent SERS behavior of adsorbates engaging in electron-transfer processes. The first systems studies were pentaammineosmium(III)/(II) bound to silver electrodes via pyridine, pyrazine, or bipyridine groups.²¹ These were selected in part because they form simple one-electron adsorbed couples, electron transfer yielding easily detectable frequency shifts in a number of vibrational modes. The potential dependence of the Os(III) and Os(II) surface concentrations determined by SERS were close to those determined by conventional electrochemistry, illustrating the utility of the technique for monitoring redox processes at electrode surface.

III. Theoretical Aspects of Electrochemical Processes

In parallel with our experimental studies of electrode processes, we have been developing theoretical models that enable the experimental data to be rationalized and interpreted at the molecular level. In view of the extensive developments in the theoretical interpretation of the kinetics of homogeneous redox processes, we have been interested in formulating methods that enable the energetics of electrochemical processes to be compared with those for structurally related processes in homogeneous solution. Some of these recent activities will now be briefly summarized. (i) We have examined various theoretical formalisms for the frequency factor of outer-sphere electrochemical reactions.¹⁸ An "encounter preequilibrium" model

has been developed which enables a particularly direct comparison to be made between the energetics of corresponding inner- and outer-sphere reaction pathways (i.e. those occurring via surface-bound and unbound transition states, respectively).

(ii) We have compared the kinetics of outer-sphere electrochemical and homogeneous reactions involving a number of aquo redox couples using the formalism noted in (i).¹¹ The results demonstrate that the energies of these processes can be quantitatively related using contemporary electron-transfer models. Very recently, we have made quantitative comparisons between the kinetics of electrochemical and related homogeneous processes with estimates obtained from contemporary theory combined with molecular structural data. (J.T. Hupp, M.J. Weaver, in preparation).

(iii) We have analyzed the theoretical significance of electrochemical activation parameters for surface-attached (or adsorbed) reactants.⁹ Application of this analysis to activation parameter data for organic-bridged Co(III) reductions has indicated the importance of electron tunneling probabilities to the observed electron-transfer rates (see above).²⁴ A related analyses applied to homogeneous intramolecular reactions has yielded a similar conclusion.²²

IV. Other Activities

We have also completed a number of other studies within the confines of the research program supported by AFOSR. Several of these have resulted in recently submitted manuscripts (see refs. 2, 10, 15, 19, 20, 25, 26 below).

Some highlights:

(i) We have examined the ability of several dicobalt cofacial porphyrins adsorbed at graphite electrodes to catalyze the four-electron reduction of

oxygen to water.¹⁹ By combining electrochemical kinetics data with e.p.r. data for the corresponding μ -superoxo porphyrin complexes, we have demonstrated that oxygen binding between the porphyrin rings in a cis configuration is responsible for the facile oxygen electroreduction pathway.

(ii) We have developed a novel "parallel simulation" scheme that enables digital simulations of coupled diffusion-heterogeneous kinetics processes to be accomplished more simply and rapidly than hitherto, using a laboratory microcomputer.¹⁰

(iii) We have demonstrated that fundamental information on the solvation of redox couples at electrochemical interfaces can be obtained from measurements of "surface reaction entropies", $\Delta S_{rc,s}^\circ$, extracted from the temperature dependence of the formal potential for adsorbed redox couples using a nonisothermal cell arrangement.^{25,26}

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1. "Electrochemical Reactions", M.J. Weaver, in "Inorganic Reactions and Methods", J.J. Zuckerman (ed), Verlag Chemie (pub), in press.
2. "The Influence of Lead Underpotential Deposition on the Capacitance of the Silver-Aqueous Interface", J.T. Hupp, D. Larkin, H.Y. Liu, and M.J. Weaver, J. Electroanal. Chem., 131, 299 (1982).
3. "The Reduction Kinetics of Pentaamminecobalt(III) Complexes Containing 4,4'-Bipyridine and Related Ligands at Mercury, Platinum and Gold Electrodes", V. Srinivasan, S.W. Barr, and M.J. Weaver, Inorg. Chem., 21, 3154 (1982).
4. "Inner-Sphere Reactivity at Solid Metal Surfaces: Adsorbed Transition-Metal Reactants at Silver, Platinum, and Gold Electrodes", K.L. Guyer, S.W. Barr, and M.J. Weaver, in "Electrocatalysis 1981", P.N. Ross (ed), Electrochemical Society (pub), Pennington, NJ, 1982, p. 377.

5. "Some Comparisons between the Energetics of Electrochemical and Homogeneous Electron-Transfer Reactions", M.J. Weaver and J.T. Hupp, in "Mechanistic Aspects of Inorganic Reactions", D.B. Rorabacher, J.F. Endicott (eds), ACS Symp. Ser., 198, 181 (1982).
6. "Determination of Specific Adsorption of Some Simple Anions at a Polycrystalline Silver-Aqueous Interface using Differential Capacitance and Kinetic Probe Techniques", D. Larkin, K.L. Guyer, J.T. Hupp, and M.J. Weaver, J. Electroanal. Chem., 138, 401 (1982).
7. "Electrochemical Reactivity at Solid Electrodes: Rate Parameters for Adsorbed Transition-Metal Reactants at the Silver-Aqueous Interface", K.L. Guyer and M.J. Weaver, J. Am. Chem. Soc., submitted.
8. "Electrochemical Reactivity at Solid Electrodes: Relative Energetics of Some Inner- and Outer-Sphere Pathways at Platinum- and Gold-Aqueous Interfaces", S.W. Barr and M.J. Weaver, J. Am. Chem. Soc., submitted.
9. "The Significance of Electrochemical Activation Parameters for Surface-Attached Reactants", J.T. Hupp, M.J. Weaver, J. Electroanal. Chem., 145, 43 (1983).
10. "A Parallel Simulation Scheme for the Rapid Accurate Calculation of Nonideal Electrochemical Transients", W.E. Schindler, Jr., M.J. Weaver, Anal. Chim. Acta, 147, 347 (1983).
11. "Electrochemical and Homogeneous Exchange Kinetics for Transition-Metal Aquo Couples: Anomalous behavior of Hexaaquo Iron(III)/(II)", J.T. Hupp, M.J. Weaver, Inorg. Chem., in press.
12. "Surface-Enhanced Raman Spectroscopy of Electrochemically Characterized Interfaces Potential Dependence of Raman Spectra for Thiocyanate at Silver Electrodes", M.J. Weaver, F. Barz, J.G. Gordon II, M.R. Philpott, Surf. Sci., 125, 409 (1983).
13. "Effect of Laser Illumination during Oxidation-Reduction Cycles upon Surface-Enhanced Raman Scattering from Silver Electrodes," F. Barz, J.G. Gordon II, M.R. Philpott, M.J. Weaver, Chem. Phys. Lett., 91, 291 (1982).
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15. "Comparisons between Theoretical and Experimental Deuterium Isotope Effects for Some Outer-Sphere Electrochemical Reactions", M.J. Weaver, T. T.-T. Li, J. Phys. Chem., 87, 1153 (1983).
16. "Specific Adsorption of Halide and Pseudohalide Ions at Electrochemically Roughened Versus Smooth Silver-Aqueous Interfaces", J.T. Hupp, D. Larkin, M.J. Weaver, Surf. Sci., 125, 429 (1983).

17. "The Influence of Experimental Nonidealities on the Determination of Rapid Electrochemical Rate Constants using Large-Amplitude Potential Steps", P.D. Tyma, E.W. Schindler, Jr., M.J. Weaver, *Anal. Chem.*, submitted.
18. "The Frequency Factor for Outer-Sphere Electrochemical Reactions", J.T. Hupp, M.J. Weaver, *J. Electroanal. Chem.*, in press.
19. "Dependence of Electrocatalysis for Oxygen Reduction by Adsorbed Dicobalt Cofacial Porphyrins upon Catalyst Structure", H.Y. Liu, M.J. Weaver, C-B. Wang, C.K. Chang, *J. Electroanal. Chem.*, 145, 439 (1983).
20. "The Nonadiabaticity Question for Europium(III)/(II): Outer-Sphere Reactivities of Eu(III)/(II) Cryptates", E.L. Yee, J.T. Hupp, M.J. Weaver, *Inorg. Chem.*, in press.
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22. "Entropic Driving Force Effects upon Preexponential Factors for Intramolecular Electron Transfer: Implications for the Assessment of Nonadiabaticity", J.T. Hupp, M.J. Weaver, submitted to *Inorg. Chem.*
23. "Surface-Enhanced Raman Spectroscopy of Electrochemically Characterized Interfaces. Relations between Raman Scattering Intensity and Surface Coverage for Simple Anionic Adsorbates", M.J. Weaver, J.T. Hupp, F. Barz, J.G. Gordon II, M.R. Philpott, *J. Electroanal. Chem.*, in press.
24. "Electron-Transfer Kinetics of Redox Centers Anchored to Metal Surfaces: Weak- versus Strong-Overlap Reaction Pathways", S.W. Barr, K.L. Guyer, T. T.-T. Li, H.Y. Liu, M.J. Weaver, in "The Chemistry and Physics of Electrocatalysis", J.D.E. McIntyre, M.J. Weaver, E. Yeager (eds), The Electrochemical Society, Pennington, NJ, in press.
25. "Redox Thermodynamics of Surface-Bound Reactants. Illustrative Behavior of Cobalt(III)/(II) Macrobicyclic "Cage" Complexes", J.T. Hupp, P.A. Lay, H.Y. Liu, W.H.F. Petri, A.M. Sargeson, M.J. Weaver, submitted to *J. Electroanal. Chem.*
26. "Utility of Surface Reaction Entropies for Examining Reactant-Solvent Interactions at Electrochemical Interfaces. Ferricinium-Ferrocene Attached to Platinum Electrodes", J.T. Hupp, M.J. Weaver, submitted to *J. Electrochem. Soc.*

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